

Thermoplastic moulding compositions.

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The thermoplastic moulding compositions according to the invention comprise partially crystalline thermoplastics and barium sulphate having a defined particle size and / or in activated surface and exhibit in increased crystallisation advises and can therefore be converted into mouldings, semifinished products and films at low mould temperatures.

Description of DE3810423

[0001] the invention concerns thermo-sculptural form masses from partial-crystalline Thermoplasten and barium sulphate by defined grain size and/or activated surface.

[0002] the use of partial-crystalline Thermoplasten, like Polyalkylenterephthalaten, in particular Polyethylenterephthalat (PET) as a form mass for the thermo-sculptural processing is hindered decisively by the fact that on account of the bad crystallisation inclination of Polyethylenterephthalat in particular high form temperatures and long cycle times are necessary to the production of hose mould parts.

[0003] to process Polyethylenterephthalat to hochwärmeformbeständigen hose downpour parts poor in delay for example applications in the electric area and electronics area economically at low form temperatures, it is necessary therefore to increase the weak crystallisation inclination of Polyethylenterephthalat.

[0004] to raise a possibility the crystallisation speed with Polyethylenterephthalat, consists in adding to the partial-crystalline Thermoplasten Nukleierungsmittel. A Nukleierungsmittel known for these purposes is, e.g., a microtalcum. Beside many other mineral Nukleierungsmitteln barium sulphate is also called. Indeed, it is put outside, for example, in the EP Os 2 15 364 on the page 1 that barium sulphate is to be counted in comparison to other inert inorganic Nukleierungsmitteln to the less effective Nukleierungsmitteln. As effective Nukleierungsmittel alkali salts of organic acids are also mentioned. Nevertheless, these have the disadvantage that partly by their basischen character often a dismantling of the PET occurs during the production and processing. Indeed, down molecular PET better crystallises, however, shows also clearly worse mechanical qualities.

[0005] now it was found astonishing that the crystallisation speed of partial-crystalline Thermoplasten, in particular from Polyethylenterephthalat, can be clearly increased by setting of certain grain dimensions and/or chemoreaktiver surfaces of barium sulphate.

[0006] now the object of the present invention thermo-sculptural form masses are over

A) To from 50.0 to 99.9 Gew. parts partial-crystalline Thermoplasten, with the exception that in case of from polyamide 6 amount to the amount in component A50 to from 98.9 or 99.1 to 99.9 Gew. parts and in case of from Polypropylen as a partial-crystalline Thermoplasten the amount in component A50 to from 59.9 or 60.1 to 99.9 Gew. parts and as a partial-crystalline Thermoplasten

B1) to from 0.1 to 50.0 Gew. parts barium sulphate with chemoreaktiver surface made by Fällung of barium ions by means of sulphate ions in watery medium in present of additional, with barium ions felleable and hardly dissolvable barium connections pedagogic Anionen of water-dissolvable connections and the preserved, if necessary with coupling means shows posttreated chemoreaktive barium sulphate grain dimensions from $<0.1 \mu\text{m}$ [80-5 m/g (to BET)], amounts with the exception that in case of from polyamide 6 as partial-crystalline Thermoplasten to the amount in component B1) from 0.1 to 0.9 Gew. parts or from 1.1 to 50 Gew. parts and in case of from Polypropylen as partial-crystalline Thermoplasten the amount in component B1) from from 0.1 to 39.9 or 40.1 to 50 Gew. parts or

B2) to from 0.1 to 50.0 Gew. parts to ultrafine barium sulphate made by bringing together separate watery solutions which contain in each case equivalent amounts of barium ions and sulphate ions, and separating the Präzipitats and one disassembles $0.1 \mu\text{m}$ in a closed reactor the watery solutions of the Reaktanden continuously in partial volumes of high number to the production of felled barium sulphate by a primary grain size from $<1 \mu\text{m}$, combines this to discreet Fällvolumina of a middle volume size from $<1 \mu\text{m}$ and leads away the educated suspension of the Präzipitats continuously from the reactor.

[0007] preferential are thermo-sculptural form masses, the component A) to from 60 to 99.9 Gew. parts and the components B1) or B2) to from 0.1 to 40 Gew. parts contain with the before described exception for polyamide 6 and Polypropylen as partial-crystalline Thermoplaste.

[0008] particularly there are preferred thermo-sculptural form masses which contain the component A) to from 99.1 to 99.9 Gew. parts and the components B1) or B2) to from 0.1 to 0.9 Gew.-to parts, with the exception of the Polyalkylenterephthalate which contain the component A) to from 95 to 99.9 Gew.-to parts and the components B1) or B2) to from 0.1 to 5.0 Gew. parts.

[0009] as partial-crystalline Thermoplasten (component A) those are possible which own while cooling the glazes with a chill rate $<1 \text{ C} / \text{Min}$ the ability to crystallise partially and which Schmelzenthalpien of from 5 to 130 J/g, prefers from 10 to 100 J/g, own. The Schmelzenthalpien of the partial-crystalline Thermoplaste can be determined, for example, after the known procedure of the differential thermo analysis, like it is described, e.g., with Vieweg/brown, plastic manual, volume I, page 591 and the following, Carl Hanser publishing company, Munich in 1975.

[0010] as partial-crystalline Thermoplasten are called, e.g.; Polyalkylenterephthalate, polyamides, Polyoxymethylen, Polyarylenoxide, Polyarylsulfide, Polyalkylene, prefers Polyethylenterephthalat, Polybutylenterephthalat, Cyclohexandimethylenterephthalat, Polyphenylsulfid, especially prefers Polyethylenterephthalat.

[0011] the possible Polyalkylenterephthalate let themselves produce publishing company, Munich in 1973) from Terephthalsäure (or her reactive derivatives) and aliphatischen Diolen with from 2 to 10 C-to atoms after known methods (plastic manual, volume VIII, page 695 and the following, Carl Hanser.

[0012] preferential Polyalkylenterephthalate contain at least 80, mainly at least 90 Mol-%, covered to the Dicarbonsäurekomponente, Terephthalsäurereste and at least 80, mainly at least 90 Mol-%, referring on the Diolkomponente, Ethylenglykol and/or Butandiol 1,4 leftovers.

[0013] the preferential Polyalkylenterephthalate can include beside Terephthalsäureresten up to 20 Mol-% of rests other more fragrantly or cycloaliphatischer Dicarbonsäuren with from 8 to 14 C atoms and/or aliphatischer Dicarbonsäuren with from 4 to 12 C atoms, like rests of Phthalsäure, Isophthalsäure, Naphthalin-2,6-dicarbonsäure, 4,4-Diphenyldicarbonsäure, amber, Adipin-, Sebacinsäure and Cyclohexandiessigsäure.

[0014] the preferential Polyalkylenterephthalate can contain beside Ethylenglykol or Butandiol 1,4 leftovers up to 20 Mol-% more different aliphatischer Diole with from 3 to 21 C atoms or cycloaliphatischer Diole with from 6 to 21 C atoms, e.g., rests of Propandiol-1,3, 2Ethylpropandiol-1,3, Neopentylglykol, Pentan-diol-1,5, Hexandiol-1,6, Cyclohexan-dimethanol-1,4, 3-Methylpentandiol-2,4, 2-Methylpentandiol-2,4, 2,2,4-Trimethylpentandiol-1,3 and -1,6, 2-

Ethylhexandiol-1,3, 2,2-Diethylpropandiol-1,3, Hexandiol-2,5, 1,4-Tu ([beta]-hydroxyethoxy) benzene, 2,2-to (4-hydroxycyclohexyl) propane, 2,4-Dihydroxy-1,1,3,3-tetramethyl-cyclobutan, 2,2-to (3-[beta]-hydroxyethoxyphenyl) propane and 2,2-to (4hydroxypropoxy-phenyl) - propan (see DE Os 24 07 674, 24 07 776, 27 15 932).

[0015] the Polyalkylenterephthalate can be branched out by installation relatively tiny amounts 3- or 4 of valued alcohols or 3- or 4-basischer carboxylic acids, as they are described, e.g., in the DE Os 19 00 270 and the US HP 36 92 744. Examples of preferential branching out means are Trimesinsäure, Trimellithsäure, Trimethylolethan and propane and Pentaerythrit. It is advisable, no more than 1 Mol-% of the Verzweigungsmittels, covered to the acid component to use.

[0016] especially Polyalkylenterephthalate which have been produced only of Terephthalsäure or their reactive derivatives (e.g., to their Dialkylestern) and Ethylenglykol are preferred.

[0017] as a component A) mainly used Polyethylenterephthalate own in the general one an Intrinsic-viscosity of from 0.4 to 1.5 DLs / gs, mainly from 0.5 to 0.8 DLs / gs, the used Polybutylenterephthalate own in the general one an Intrinsic viscosity of from 0.7 to 1.6 DLs / gs, mainly from 0.8 to 1.3 DLs / gs, in particular from 0.8 to 1.05 DLs / gs, in each case measured in phenol / o-Dichlorbenzol (1: 1 Gew. parts) with 25 C.

[0018] as a component A) to possible partial-crystalline polyamides enclose langkettige synthetic polymers which own regularly returning Amidgruppen as an integral component of the main polymer chain and enclose therefore Amidestermischpolymere. They are described in the plastic manual, volume VI, Carl Hanser publishing company, Munich. Polyamides can be produced by polycondensation or addition difunktioneller Monomere or cyclischer Lactame (as for example from [epsilon]-Aminocapronsäure or [epsilon]-Caprolactam) or by conversion of a conjugated monomer pair, as for example of a Diamins and a Dicarbonsäure.

[0019] preferential partial-crystalline polyamides are able to by Polymerisation of Lactamen of the formula

[image - see original document]

are produced in what R an Alkylengruppe with from 3 to 13 or more carbon atoms, mainly with from 5 to 13 carbon atoms, signifies. Preferential Lactame are [epsilon]-Caprolactam, Pyrrolidon, Piperidon, Valerolactam, Capryllactam and Lauryllactam. Also mixing polyamides from two or several Lactamen are enclosed. The preferential polyamine which is useful to the production of polyamides is, for example, Propandiamin, Hexamethylendiamin and Octamethylendiamin. Preferential polycarboxylic acids are, for example, an adipic acid, Pimelinsäure, Suberinsäure, Sebacinsäure and Dodecansäure.

[0020] preferential partial-crystalline polyamides enclose, e.g., polyamide 6, polyamide 6.6, which mixtures, block polyamides and Copolyamide from [epsilon]-Caprolactam, adipic acid and Hexamethylendiamin, furthermore polyamide 11, polyamide 12 and polyamides which are built up from aliphatischen slide mines and adipic acid and/or Isophthalsäure and/or Terephthalsäure and/or Sebacinsäure and/or Azelainsäure and/or Cyclohexandicarbonsäure.

[0021] as an aliphatische slide mine are to be called except Hexamethylendiamin, 2,2,4-and 2,4,4Trimethyl-hexamethylendiamin, Isophorondiamin, 1,3-and 1,4Bis-aminocyclohexan, Bisaminocyclohexyl-alkane and Xylylendiamine.

[0022] in addition, partial-crystalline polyamides are considered which are produced of called aliphatischen to Dicarbonsäuren and aromatic slide mines as for example m- and p-Phenylendiamin, as well as polyamide mixtures and Copolyamide, from all called components, as far as aliphatische or teilaliphatische polyamides originate. Especially preferential polyamides are aliphatische polyamides, in particular polyamide 6 and Polyamid-6,6.

[0023] preferential polyamides own a relative viscosity of from 2.0 to 6.0, mainly from 2.5 to 4.5, measured in a solution of 0.5 gs of polyamide in 100 ml m-Kresol-solution with 25 C.

[0024] as a component A) possible Polyoxymethylene certain molecular weights of from 20,000 to 100,000, mainly from 30,000 to 50, 000 own as figure means. They are described in the plastic manual, volume XI, Carl Hanser publishing company, Munich.

[0025] as a component A) possible Polyalkylene, e.g., Polyethylen and Polypropylen, can be produced after high-level procedure, middle procedure and low pressure procedure and own in the general molecular weight certain as figure means of from 20,000 to 500,000, mainly from 50,000 to 350,000. They are described in the volume IV of the plastic of manual.

[0026] as a component A) possible Polyarylsulfide, e.g., the Polyphenylensulfid, can be

produced after known procedures (cf., e.g., the US 33 54 129 and EP 1 71 021). As a component A) possible Polyarylenoxide are described like in the literature (H.M. van Thère et al., European. Polym. J. 4, 275 (1968)) made.

[0027] as a component B1) of the erfindungsgemässen thermo-sculptural form masses can be used barium sulphate with chemoreaktiver surface made by Fällung of barium ions by means of sulphate ions in watery medium in present of additional and hardly dissolvable barium connections felleable with barium ions pedagogic Anionen of water-dissolvable connections and the preserved chemoreaktive barium sulphate grain dimensions from $<0.1\text{ }\mu\text{m}>$, prefers from 0.09 to $0.01\text{ }\mu\text{m}$ (from 80 to $5\text{ }\mu\text{m}>/\text{g}$ prefers from 50 to $10\text{ }\mu\text{m}>/\text{g}$, (to BET)) shows.

[0028] with the failure of barium sulphate in the present of Anionen which with barium ions hardly dissolvable connections form suitable concentrations preserved product, contains the foreign ions either homogeneous about the crystal distributed or this in the surface fortified.

[0029] according to load density and molecule size of the anion or doping components defects are taken in the BaSO_4 -crystal grid or grid places are taken in statistical distribution or there occurs with long apolaren molecule leftovers a screening of the surface load (Hydrophobierung).

[0030] according to the procedure Anionen can be used more water-dissolvably of organic or inorganic connections. In some cases it can be also suitable to use mixtures of these connections.

[0031] for the realisation of the procedure these additional components are added suitably to the watery solution which contains the inorganic sulphate component, like alkali sulphate. The additional component becomes in an amount from 0.1 to 50 Gew.-%, covered to the barium sulphate to be felled, used. Mainly the additional component is used in an amount from 1 to 10 Gew.-%.

[0032] suitable organic water-dissolvable connections for the procedure are connections from the group Alkyl- and Arylsulfonate, Alkyl- and Arylsulfate or Alkyl- and Arylphosphorsäureester and Alkyl- or Arylrest can be partially substituted if necessary for functional groups, or perfluorierte Alkyl- and Arylsulfonate. For example, are used in the procedure of the invention:

Natriumdodecylbenzolsulfonat

Natriumlaurylsulfat

Natriumcetylsulfat

Phosphorsäuremonoethylmonobenzylester

Lithiumperfluorooctansulfonat.

[0033] as the connections which carry with functional groups substituted Alkyl- or Arylreste those are suited with halogen, hydroxyl, Amino-, Imino- or Mercapto-groups or a final-constant double connection, for example

12-Brom-1-dodecansulfonsäure

Natrium-10-hydroxy-1-decansulfonat

Natrium-Carrageenan

Natrium-10-Mercapto-1-Cetansulfonat

Natrium-16-Ceten (1) sulfat.

[0034] in the procedure to the production from chemoreaktivem Bariumsulfat inorganic connections from the group Thiosulfat, silicate, Fluorid, fluorine silicate, mono fluorine phosphate or Wolframmat are used as an Anionen more water-dissolvably of inorganic connections (other inorganic connections than sulphates). Suitable connections are, for example

Natriumthiosulfat ($\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$)

Sodium silicate (Na_2SiO_3)

Natriumfluorid (NaF)

Lithiumhexafluorosilikat ($\text{Li}_2(\text{SiF}_6) \cdot 2\text{H}_2\text{O}$)

Natriumfluorophosphat ($\text{Na}_2\text{PO}_3\text{F}$)

Natriumpolywolframmat ($3\text{Na}_2\text{WO}_4 \cdot 9\text{H}_2\text{O}$).

[0035] the chemoreaktiven barium sulphate pigments made after the procedure can find out an aftercare suitable for the intended intended purpose.

[0036] if are of the barium sulphate surface, e.g., by the doping components sour or veresterbare hydroxyl groups, how

[image - see original document]

impressed or are in the Kristallitoberfläche beside the (SO_4) $<2>$ - Anionen by Copräzitation

introduced, other chemically moveable groups, like S-, SH- or F- , this BaSO_4 pigment can be equipped with suitable aftercare components or coupling means for the respective operational area. One in the general used custody mediator or coupling means are organofunktionelle Alkoxysilane, how Vinyltrimethoxysilan. However, it are also used Alkoxytitanate, -zirkonate or -aluminat. The application of the custody mediator occurs in way known in itself. He can be raised in a solvent relaxedly on the pigment and the solvent is drawn off and the solid is dried. Or the allocation occurs with liquid custody mediators through Verdüsen. By means of on the pigment powder moved in the mixing bed.

[0037] as a component B2) of the thermo-sculptural form mass ultrafine barium sulphate to be added is produced by bringing together separate watery solutions which contain in each case equivalent amounts Bariumion or Sulfation, and separating the Präzipitats and one disassembles 1 m in a closed reactor the watery solutions of the Reaktanden continuously in partial volumes of high number to the production of felled barium sulphate by a primary grain size from $<$, combines this to discreet Fällvolumina of a middle volume size from <1 l and leads away the educated suspension of the Präzipitats continuously from the reactor. In the watery solution of the Sulfations another anion can be also contained more water-dissolvably of inorganic or organic connection which forms treacly dissolvable barium connections.

[0038] after the procedure small partial volumes of the reaction solutions are brought together therefore in high number, for example, more than 10 $<6>$ per sec, and are caused in a reaction volume of a middle volume size from <1 l the Fällung quickly and completely.

[0039] for the realisation of the procedure the respective watery solutions of the Reaktanden are continuously quickly brought together in each case in drop shape of a middle drop size from <0.5 l and are combined in a Fällvolumen of a middle volume size from <1 l.

[0040] after an other arrangement of the procedure one would cross the watery solution of one Reaktanden continuously in a drop shape of a middle drop size from <0.5 l and introduces these drops continuously in a fluent film of the watery solution of the other Reaktanden.

[0041] that is in other words, it droplets of the watery solution of one Reaktanden are brought together with droplet of the other Reaktanden at high speed, or these become the droplets of the watery solution of one Reaktanden in the fluent film of the watery solution of the other Reaktanden at high speed eingeschleudert, for example, the droplets of a watery barium chloride solution in the Rieselfilm of a watery sodium sulphate solution.

[0042] the procedure is carried out suitably in a vertical, cylinder-shaped closed reactor. The reactor shows, on this occasion, in his head part in itself known means or devices to the cerium division of watery component solutions in the finest droplets, as well as means to the production of a Rieselfilms from watery component solutions. In his ground part a such reactor is formed suitably conical and is provided with deduction facilities for the reaction mixture or for the Fällungssuspension.

[0043] the drop shape of the reaction solution is able to in the head part of the cylindrical reactor by Zerstäubung of the solution under pressure, for example, nozzles, or are generated by effect of centrifugal strength on the solution, for example, atomizer discs. The droplets have a size from <0.5 , mainly from 0,001 to 0.25 l. The Rieselfilm in the inner wall of the reactor is generated in a thickness of 1 to 10 mms.

[0044] the droplet streams of the watery solutions can be directed diametrically or in a corner mutually. The droplet streams can be led furthermore, however, also in parallel in the same direction in the reactor and be brought to the mutual penetration and Fällung.

[0045] the film running off in the reactor wall of the Fällungssuspension is collected in the lower part of the reactor and is delivered about a Dosiervorrichtung from the reactor and on the solid, from 0.09 to 0.01 (surface (BET) prefers like ultrafine barium sulphate of a primary grain size under 0.1: From 80 to 5 m $<2>/g$, prefers from 40 to 10 m $<2>/g$) worked off.

[0046] the addition of the barium sulphate with chemoreaktiver surface or the ultrafine barium sulphate can occur at every time of the Thermoplast production. The addition of the components B) is preferred in form of a Slurry from the (@) reaction partner (n) or an inert reaction solvent at every time of the reaction. For example, a BaSO_4 /Ethylenglykol-Slurry, at every time of the reaction can be added with the Polyalkylenterephthalatsynthese BaSO_4/C_2 -to C_8 -Alkandiol-Slurry, especially preferential to the production erfindungsgemässer Polyethylenterephthalate. However, it is also to be added possibly the component B) in form of a highly concentrated

Compounds to the Schmelzcompoundierung.

[0047] the erfindungsgemässen thermo-sculptural form masses can contain usual processing aids like Assembly-line and Entformungsmittel, filling means and strengthening means, like talc, chalk and fibreglasses, organic fibers, pigments like Titandioxid and soot, fire prevention means, like halogen connections, Antimontrioxid, and stabilizers, like down molecular Phosphite. Also alloys with other Thermoplasten can be produced with erfindungsgemässen, to partial-crystalline, nukleierten Thermoplasten after known procedures as for example glaze extruding.

[0048] the usual processing aids are added to the form masses in an effective amount managing for the respective purpose.

[0049] the erfindungsgemässen thermo-sculptural form masses can be processed to form bodies, half witnesses and foils.

[0050] the erfindungsgemässen thermo-sculptural form masses own the advantage that they can crystallise more quickly and be processed, therefore, at low form temperatures (no oil-heated forms) or with clearly shorter hose cycles. On this occasion, result schwindungsarme form parts with high warm form permanence. In particular so preserved form masses PET distinguish themselves in comparison to PET masses conventionally preserved with known Nukleierungsmitteln by high Vicat B values.

Auführungsbeispiel

Examples

Component A

Polyethylenterephthalat (PET)

[0051] PET will receive after reaction from Dimethylterephthalat (DMT) and Ethylenglykol (EC) and next polycondensation. Besides, mol relations of DMT are possible to the EC of 1.0 to from 1.2 to 3.5. Besides, as catalysts are possible connections of the elements Mn, mg, Sb, Zn, Co and a. as well as combinations of these elements. An addition of the component B1 or B2 can occur practically at every time of the reaction.

Typical beginning

[0052] 5825 gs Dimethylterephthalat, 4656 gs Ethylenglykol and 287.2 gs 10.1 Gew.-% bariumsulfathaltige Ethylenglykollurly as well as 4.26 gs Titantetraisopropylat are heated up after rinse of the apparatus with nitrogen within 1 h on 180 C and are held at this temperature. Then the temperature on 190 C is raised for 1.5 h. Within other 1.5 h an other temperature rise on 250 C occurs. After 15 min at this temperature the pressure on <1 mbar is degraded and überschüssiges Ethylenglykol abdestilliert. Within 30 the temperature on 275 C is increased min and approx. 30 leave - 60 min there. On ventilating the apparatus with nitrogen and setting down the glazes becomes abgesponnen.

[0053] yield: 4843 gs (85%) Polyethylenterephthalat, I. V. 0.71.

Components B1) and B2)

Example 1

a) To the production of a barium sulphate with chemoreaktiver surface (according to component B1) were brought in a Fällzelle under stirring a barium chloride solution with a sodium sulphate solution to the reaction. Before the conversion the Na₂SO₄ solution (density 1,088 gs / ml) with 7 gs Natriumhydroxid per litre of Na₂SO₄ solution was put alkaline and moved then with 32 gs of Na₂SiO₃ solution (density 1,346 gs / ml) per litre of sulphate solution. In the device 105.7 ml/min BaCl₂ solutions (density 1,073 gs / ml) and 896 ml/min of the silicate-containing Na₂SO₄ solution were put through. The precipitation was dried abfiltriert, several times with water washed and with 110 C. The wet-chemical analysis of the dry product proved a SiO₂ content of 0.62%. The BET surface of the product amounted to 18.3 m²/g.

b) For the purpose of surface modification of one after a) made silicate-containing barium sulphate with a vinyl grouping this became in anhydrous Isopropanol dispergiert (solid salary 10

Gew.-%). Under touching 1%ige solution of Vinyltrimethoxysilan became in anhydrous Isopropanol in an amount zugetropft that in the Anschlammung 0.5.Gew.-% of the Silans, covered to the pigment, were. The dispersion was stirred approx. 1 hour with approx. 40 C and then abfiltriert. Afterwards unused physisorptiv engaged Silan was washed out with anhydrous Isopropanol from the solid and was dried latter. It attacked a BaSO₄, on the IR-spektroskopisch the vinyl grouping could be proved.

Example 2

[0054] of purpose Fällung of an ultrafine barium sulphate (according to component B2) from watery solutions of barium chloride and sodium sulphate by means of a Verdüsungsvorrichtung sodium sulphate solution of the density 1,033 gs / ml became in a closed, vertical cylindrical reactor (diameter 300 mms) by a ring nozzle in such way eingepumpt that a fluent thin case film on the inner wall of the reactor originated. The supply of the barium chloride solution (density 1,162 gs / ml) occurred below the ring nozzle about a concentrically arranged centrifugal atomizer wheel with radial canals with 40,000 Upm. In the Rieselfilm a Fällvolumen of smaller than 0,001 cm ³ was achieved in each case by the droplets. The educated barium sulphate suspension was caught in the lower tube end, was released from the mother's lye, washed and dried with 110 C. With a Molverhältnis sodium sulphate: Barium chloride of 1: 0.7 and the Durchsätzen 0.83 mol/min barium chloride or 1.19 mol/min sodium sulphate an ultrafine barium sulphate of a grain size of 0.07 m was won. The regulation of the specific surface to BET in the powder product proved a value of 33 m ²/g.

Example 3

[0055] the Fällung of an ultrafine barium sulphate (according to component B1 and B2) from a watery solution of sodium sulphate and a watery Natriumlaurylsulfat containing sodium sulphate solution was carried out in an atomizer device. Moreover two atomizer nozzles were so arranged in a closed, cylindrical, vertical reactor that themselves her escape openings subtended in a distance of 500 mms and formed the spray cones in the vertical contact surface a congruent circle. A watery barium chloride solution (density of 1,050 gs / ml) was sprayed by one nozzle with an atmospheric pressure of 6 cash, while at the same time by the other nozzle a sodium sulphate solution, containing 2.5 gs Natriumlaurylsulfat per litre of Na₂SO₄ solution (density of 1,104 gs / ml) and a pressure of 3.2 was sprayed cash.

[0056] it was put through 44.2 l/h of the Natriumlaurylsulfat containing sodium sulphate solution and 81.8 l/h barium chloride solution. The educated barium sulphate suspension was caught, released from the mother's lye, dried several times with water washed up to a conductivity of the suspension by 100 p. / cm and then with 110 C. The carbon regulation of the dry product proved a carbon salary of 0.32%. The regulation of the specific surface of the powder product to BET proved a value of 36 m ²/g. This corresponds to a primary grain size of 0,038 m.

Example 4

[0057] purpose production of an ultrafine, low-salt barium sulphate (according to component B2) the Fällung was carried out in an atomizer device by conversion of a Bariumhydroxidlösung with sulfuric acid.

[0058] of an audacious out of vision atomizer nozzle which was fastened centrally in the lid of a closed, vertical, cylindrical reactor Bariumhydroxidlösung (density 1,160 gs / ml with 75 C) and sulfuric acid (density 1,060 gs / ml with 25 C) with a pressure of 3.3 was sprayed cash. Both Reaktanden met in the nozzle mouth in a circular full cone. It was put through 12.6 l/h Ba (OH) ₂ solution and 12.3 l/h sulfuric acid. The resulted BaSO₄ suspension was caught, the pH factor on from 6.5 to 7.0 was put, the Fällprodukt was separated and dried with from 110 to 120 C.

[0059] the specific surface of the dry product to BET proved a value of 51.5 m ²/g. This corresponds to a primary grain size of 0,026 m.

Thermo-sculptural form masses

[0060] suitable thermo-sculptural form masses can be received:

1. After for component A) given regulation (if necessary training of usual processing aids by

extruding).

2. By glaze extruding after 1. preserved component A) as a highly concentrated BaSO₄ / PET with commercially available PET.

3. In similar way other partial-crystalline Thermoplaste with improved crystallisation inclination can be produced.

[0061] the following results will receive it:

[image - see original document]

[0062] the results show in the table that with comparable viscosity level the barium sulphates (B1 as well as B2) deliver higher Vicat B values in comparison to usual Nukleierungsmittel clearly.

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Claims of DE3810423

1. Thermo-sculptural form masses from

A) To from 50.0 to 99.9 Gew. parts partial-crystalline Thermoplasten, with the exception that in case of from polyamide 6 amount to the amount in component A 50 to from 98.9 or 99.1 to 99.9 Gew. parts and in case of from Polypropylen as a partial-crystalline Thermoplasten the amount in component A 50 to from 59.9 or 60.1 to 99.9 Gew. parts and as a partial-crystalline Thermoplasten

B1) to from 0.1 to 50.0 Gew. parts barium sulphate with chemoreaktiver surface made by Fällung of barium ions by means of sulphate ions in watery medium in present of additional, with barium ions felleable and hardly dissolvable barium connections pedagogic Anionen of water-dissolvable connections and the preserved, if necessary with coupling means shows posttreated chemoreaktive barium sulphate grain dimensions from <0.1 µm [80-5 m/g (to BET)], amounts with the exception that in case of from polyamide 6 as a partial-crystalline Thermoplasten to the amount in component B1) from 0.1 to 0.9 Gew. parts or from 1.1 to 50 Gew. parts and in case of from Polypropylen as a partial-crystalline Thermoplasten the amount in component B1) from from 0.1 to 39.9 or 40.1 to 50 Gew. parts or

B2) to from 0.1 to 50.0 Gew. parts to ultrafine barium sulphate made by bringing together separate watery solutions which contain in each case equivalent amounts of barium ions and sulphate ions, and separating the Präzipitats and one disassembles 0.1 µm in a closed reactor the watery solutions of the Reaktanden continuously in partial volumes of high number to the production of felled barium sulphate by a primary grain size from <, combines this to discreet Fällvolumina of a middle volume size from <1 l and leads away the educated suspension of the Präzipitats continuously from the reactor.

2. Thermo-sculptural form masses after claim 1, thereby marked that as partial-crystalline Thermoplasten those are used which crystallise 1 °C / while cooling the glazes with a chill rate from <Min partially and own Schmelzenthalpien of from 5 to 100 J/g.

3. Thermo-sculptural form masses after claims 1 and 2, thereby marked that one starts as partial-crystalline Thermoplasten Polyalkylenterephthalat, polyamides, Polyalkylene, Polyoxymethylen, Polyarylsulfide or Polyarylenoxide.

4. Thermo-sculptural form masses after claims from 1 to 3, thereby marked that one starts as partial-crystalline Thermoplasten Polyethylenterephthalat, Polybutylenterephthalat, Cyclohexandimethylenterephthalat or Polyphenylensulfid.

5. Thermo-sculptural form masses after claims from 1 to 4, thereby marked that one starts as a partial-crystalline Thermoplast Polyethylenterephthalat.

6. Thermo-sculptural form masses after claims from 1 to 5, thereby marked that as a component B1) used barium sulphate with chemoreaktiver surface is produced in present by organic water-

dissolvable connections of the group Alkyl-and Arylsulfonate, Alkyl-and Arylsulfate, Alkyl-and Arylphosphonsäureester and Alkyl- or Arylrest can be partially substituted if necessary for functional groups, perfluorierte Alkyl-and Arylsulfonate or in present of Anionen more water-dissolvably of inorganic connections from the group Thiosulfat, silicate, Fluorid, fluorine silicate, mono fluorine phosphate or Wolframat and the barium sulphate is posttreated if necessary with coupling means.

7. Thermo-sculptural form masses after claims from 1 to 6, thereby marked that one adds the barium sulphate B1) or B2) with the reaction partners or a suitable reaction mixture in a highly concentrated Slurry at every time of the polymer synthesis.

8. Thermo-sculptural form masses after claims from 1 to 7, thereby marked that a barium sulphate (B1 or B2)/C2-to C8-Alkandiol-Slurry is used.

9. use of the thermo-sculptural form masses after claims from 1 to 6 to the production of form bodies, half witnesses and foils.